



D010312

March 12, 2001

To Sumitomo Rubber Industries Limited
Intellectual Property Division
Atsuro SUMITOMO

Sankyo Patent Attorneys Office
Eriko KAMITANI

Dear Sir, I'm glad to hear that things are going well
for you.

Now, I have prepared a specification (corrected
version) of your case No.K1010014 (Our case
No.28307). I would like you to check it.

Moreover, regarding the mixing ratio of OH or amino
group to isocyanate, there is confusion between the
case of isocyanate being denominator and the case
of OH group and the like being denominator. Please
confirm them again.

[Kind of document] SPECIFICATION

[Title of the Invention] GOLF BALL HAVING A
URETHANE COVER

[Claims for the Invention]

[Claim 1] In a golf ball comprising a core and a polyurethane cover covering the core, the golf ball is characterized in that:

the polyurethane cover is formed from a cured product by curing a urethane prepolymer having an isocyanate group at a terminal thereof with a curing agent; and

the polyol component constituting the urethane prepolymer is a polycarbonate polyol having a number-average molecular weight of from 300 to 3000.

[Claim 2] The golf ball according to claim 1, wherein the polycarbonate polyol is poly(hexamethylene carbonate) or poly(1,4-cyclohexamethylene carbonate).

[Claim 3] The golf ball according to claim 1 or 2, wherein

the urethane prepolymer has a free NCO group content of from 5 to 15% by mass; and

the curing agent is a diol or a diamine having a number-average molecular weight of from 50 to 500, and is used in an amount such that the equivalent

ratio of the amino group or hydroxyl group of the curing agent to the free isocyanate group of the urethane prepolymer (OH/NCO or NH₂/NCO) ranges from 0.8 to 1.2.

[Claim 4] The golf ball according to any one of claims 1 to 3, wherein the polyurethane cover has a Shore D hardness of from 40 to 63 at a non-dimpled portion thereof.

[Detailed Description of the Invention]

[Industrial Field of the Invention]

The present invention relates to a golf ball covered with a thermosetting polyurethane cover that enables to maintain a high repulsion property even if the ball is left under a severe condition such as in a rainy weather, in a heat wave, or under a burning sun.

[Prior Art and Problems which the Invention Solves]

Ionomer resin covers are mainly used for golf ball covers because they have superior durability. Such ionomer resin covers, however, give golfers a larger impact upon a shot than Balata covers, and hence are likely to impart the golfers with an inferior shot feeling.

In attempt to improve the shot feeling imparted by ionomer covers, Japanese Patent No. 2709950, for

example, has proposed a mixed ionomer cover, which is a mixture of a hard ionomer of sodium salt or zinc salt of an olefin-unsaturated carboxylic acid copolymer and a soft ionomer of sodium salt or zinc salt of an olefin-unsaturated carboxylic acid-unsaturated carboxylate terpolymer. Blending the soft ionomer enables to make the shot feeling soft, but on the contrary, the merits inherent in ionomer covers will be impaired. For example, the repulsion property as well as the scuff resistance (or chunking property) of the golf ball upon a shot will be lowered.

In recent years, polyurethane is receiving attention as an inexpensive cover material that imparts a shot feeling analogous to the Balata cover and has higher durability than the Balata cover. Japanese Patent No. 2662909, for example, has disclosed a polyurethane cover cured by curing a urethane prepolymer with a slow-reactive polyamine curing agent.

Japanese Patent No. 2662909 teaches a urethane prepolymer obtained by reacting a polyol such as polyether polyol, polyester polyol or polylactone polyol with a diisocyanate such as 4,4'-diphenylmethane diisocyanate (MDI), or

3,3'-dimethyl-4,4'-biphenylene diisocyanate
(TODI).

Generally, the performance of the polyurethane resin significantly depends on the soft segment constituting the polyurethane. The component corresponding to the soft segment of polyurethane is a polyol constituting a urethane prepolymer. The Japanese Patent, however, is completely silent on the relation between the polyol used and a resultant polyurethane cover or a resultant golf ball. Meanwhile, it is likely that golf balls, which are observed to have not so large a difference in performance therebetween when they are each in a brand-new state, come to exhibit a considerable difference in performance therebetween if they are left under a severe condition such as in a rainy weather, in a heat wave, or under a burning sun.

The present invention has been achieved in view of the above circumstances. It is an object of the present invention to provide a golf ball having a thermosetting polyurethane cover that can maintain its ball characteristics even in a severe condition such as in a rainy weather, in a heat wave or under a burning sun.

[Means by which the Problem is Solved]

A golf ball of the present invention is a golf ball comprising a core and a polyurethane cover covering the core, wherein the polyurethane cover is formed from a cured product by curing a urethane prepolymer having an isocyanate group at a terminal thereof with a curing agent, and a polyol component constituting the urethane prepolymer is a polycarbonate polyol having a number-average molecular weight of from 300 to 3000.

The polycarbonate polyol is preferably poly(hexamethylene carbonate) or poly(1,4-cyclohexamethylene carbonate).

It is preferable that the urethane prepolymer has a free NCO group content of from 5 to 15% by mass; and that the curing agent is a diol or a diamine having a number-average molecular weight of from 50 to 500, and is used in an amount such that the equivalent ratio of the amino group or hydroxyl group of the curing agent to the free isocyanate group of the urethane prepolymer (OH/NCO or NH₂/NCO) ranges from 0.8 to 1.2.

It is also preferable that the polyurethane cover has a Shore D hardness of from 40 to 63 at a non-dimpled portion thereof.

[Embodiments of the Invention]

The golf ball of the present invention is characterized in being covered with a polyurethane cover using a urethane prepolymer containing a specific polyol component.

First, the polyurethane cover used in the present invention will be described. The polyurethane cover used in the present invention is formed from a cured polyurethane product by curing a urethane prepolymer having an isocyanate group at a terminal thereof (hereinafter referred to as "isocyanate-terminated urethane prepolymer") with a curing agent, wherein the urethane prepolymer is obtained by reacting a polycarbonate polyol with an isocyanate.

The use of a polycarbonate as a polyol component that forms the soft segment of the resulting polyurethane that constitutes the cover allows to provide a golf ball that is less susceptible to changes in its characteristics even under a severe environmental condition such as in a rainy weather, in a heat wave or under a burning sun, and hence exhibits superior durability. The polyol constituting the urethane prepolymer crystallize more easily, and hence shows higher repulsion property and durability, as the linearity and

symmetry of the molecular chain thereof become higher. A golf ball manufactured using a polyether polyol or polyester polyol exhibits a superior repulsion property due to the high crystallinity when it is in a brand-new state. However, ester bonds or ether bonds tend to be decomposed with heat or to be hydrolyzed, thus the macropolyol will be decomposed, the crystallinity thereof will be lowered and the physical properties of the resultant golf ball will be lowered if the golf ball is left under a severe condition such as in a rainy weather, in a heat wave or under a burning sun. A polycarbonate polyol, on the other hand, is less susceptible to hydrolysis or thermal decomposition than the ether bond and ester bond, thus is capable of maintaining a superior repulsion property in a brand-new state for a long time.

Such a polycarbonate polyol for use in the present invention has a number-average molecular weight of not less than 300, preferably not less than 900, more preferably not less than 1600. The upper limit of the number-average molecular weight thereof is not more than 3000, preferably not more than 2900. If the number-average molecular weight is less than 300, the soft segment of the resulting

polyurethane is relatively small, and hence a golf ball exhibits an insufficient repulsion property even when it is in a brand-new state. Further, such a small soft segment makes the resultant polyurethane too hard, resulting in a poor shot feeling and an inferior controllability. On the other hand, if the number-average molecular weight is more than 3000, the polycarbonate polyol has such a high viscosity as to lower the workability thereof in mixing and reaction with a diisocyanate. Further, the melting point of the polycarbonate polyol becomes higher with increasing molecular weight. Therefore, the molding of a cover, during which the reaction between the urethane prepolymer and the curing agent proceeds, needs to be performed at a higher temperature. The curing reaction at such a high temperature proceeds too rapidly, and hence the cover composition exhibits lowered workability. In addition, the molding at such a high temperature causes the deterioration of the rubber core.

The term "number-average molecular weight", as used in the present invention, is a polystyrene-converted value measured by gel permeation chromatography (GPC).

The polycarbonate polyol may be any diol

represented by the general formula: $\text{HO}-(\text{ROCO})_n-\text{ROH}$ but is preferably poly(hexamethylene carbonate) of which R is represented by the following formula (1) or poly(1,4-cyclohexanedimethylene carbonate) of which R is represented by the following formula (2).

[Formula 1]

Poly(hexamethylene carbonate) and poly(1,4-cyclohexanedimethylene carbonate) are preferable because they are excellent in heat resistance, hydrolysis resistance and weather resistance.

The polyol used as a raw material of the isocyanate-group terminated urethane prepolymer may comprise any polyol other than the polycarbonate polyol, as long as the amount thereof to be used is less than 45% by mass based on the total amount of the used polyol. In a preferable embodiment, all of the polyol component is the polycarbonate polyol.

Examples of usable polyols other than the polycarbonate polyol include low-molecular-weight diols such as ethylene glycol, diethylene glycol, triethylene glycol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, and 1,6-hexanediol; low-molecular-weight triols such as glycerin, trimethylolpropane, and hexanetriol; and polymer

polyols such as polyether polyol, polyester polyol, lactone type polyester polyol, and acrylic polyol.

Examples of the polyisocyanate compound for use as a raw material of the isocyanate group-terminated urethane prepolymer include, without any particular limitation, aromatic diisocyanates such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and a mixture (TDI) of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 1,5-naphthylene diisocyanate (NDI), 3,3'-bitolylene-4,4'-diisocyanate (TODI), xylylene diisocyanate (XDI) and paraphenylene diisocyanate (PPDI); and alicyclic or aliphatic diisocyanates such as 4,4'-dicyclohexylmethane diisocyanate (hydrogenated MDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), or mixtures of at least two of them. Among them, TDI or MDI is preferably used because the resulting polyurethane cover has favorable mechanical properties and a golf ball with the resulting polyurethane cover is satisfactory in repulsion property, weather resistance and water resistance.

The isocyanate-terminated urethane prepolymer is

obtained by mixing the polyisocyanate compound and a polyol comprising the above polycarbonate polyol so that the molar ratio of OH group:NCO group ranges from : to : and allowing them to react with each other.

The free NCO content of the isocyanate-terminated urethane prepolymer used in the present invention is from 3 to 20% by mass, preferably from 5 to 15% by mass. Since free NCO becomes a reaction site for the curing agent, free NCO has a relation with the crosslinking density of the resulting polyurethane. If the free NCO content is less than 3% by mass, the resulting polyurethane is so soft that repulsion will be lowered. Thus, when a ball is hit with a golf club, the ball departs from the club with a delay so that the golfer feels it heavy. If it is more than 20%, the resulting polyurethane is so hard that the repulsion will be enhanced. But the impact given to the golfer upon shot will be too large.

As the curing agent used for curing the urethane prepolymer, there may be used a polyol compound having an alcoholic hydroxyl group, an amine compound, or a mixture of them, without any particular limitation.

Such an amine-type curing agent is preferably an aromatic polyamine compound having at least two amino groups bonded to an aromatic ring. For example,

3,3'-dichloro-4,4'-diaminodiphenylmethane, methylenedianiline, a complex of methylenedianiline and sodium chloride, 1,2-bis(2-aminophenylthio)ethane, 3,5-dimethylthio-2,4-toluenediamine, 3,5-dimethylthio-2,6-toluenediamine, trimethylene glycol-di-p-aminobenzoate, and polytetramethyleneoxide-di-p-aminobenzoate can be used. Such polyol-type curing agent includes a polyol compound such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, pentanediol, hexanediol, bishydroxybenzene, trimethylolpropane, and pentaerythritol.

Preferably, the urethane cover composition used in the present invention is prepared by mixing the curing agent and the urethane prepolymer so that the equivalent ratio of the total of the amino group and hydroxyl group of the curing agent to the free isocyanate group of the urethane prepolymer, i.e., $\{(\text{OH or NH}_2)/\text{NCO}\}$ ranges from 0.80 to 1.2. Particularly when an isocyanate-terminated

urethane prepolymer having a free NCO content of 3 to 20% by mass is used, it is preferred that a diol or diamine curing agent having a molecular weight of from 50 to 500 is used as the curing agent and that they are mixed and reacted so that the equivalent ratio of the amino group or hydroxyl group of the diamine or diol to the free isocyanate group, i.e., OH/NCO or NH₂/NCO, ranges from 0.8 to 1.2.

The polyurethane cover composition used in the present invention may contain a catalyst conventionally known for use in a urethane reaction in addition to the urethane prepolymer and the curing agent described above. Examples of the catalyst include monoamines such as triethylamine and N,N-dimethylcyclohexylamine; polyamines such as N,N,N',N'-tetramethylethylenediamine and N,N,N',N'',N''-pentamethyldiethylenetriamine; cyclic diamines such as 1,8-diazabicyclo[5,4,0]-7-undecene (DBU) and triethylenediamine; and tin catalysts such as dibutyltin dilaurylate and dibutyltin diacetate.

As required, the polyurethane cover composition may further contain a filler such as barium sulfate, a coloring agent such as titanium

dioxide, and additives such as a dispersant, antioxidant, ultraviolet absorber, light stabilizer, fluorescent material, and fluorescent brightener unless they impair the desired properties of an intended golf ball cover.

As a process for preparing the polyurethane cover, any conventionally known process can be employed. The urethane cover composition are mixed using a mixer having a typical stirring ability, and then the resulting polyurethane cover composition is injected into a hemispherical mold holding a core and allowed to cure therein. Though there is no limitation on mixing process, it is preferred that the composition be sufficiently stirred by the use of a two-part resin mixing dispenser or the like so as not to include air therein.

The polyurethane cover thus manufactured preferably has a Shore D hardness (ASTM D-2240) of from 40 to 63 at a non-dimpled portion thereof, in a state of the ball. If it is less than 40, the cover is so soft as to lower the scuff resistance as well as the repulsion property of the ball. If it is more than 63, the cover is so hard, resulting in the harder shot feeling and lowered spin performance.

There is no particular limitation on the core

used for the golf ball of the present invention. It is possible to use a solid core conventionally used in a multi-piece solid golf ball or any conventional wound core.

The solid core is a vulcanized body of a core rubber composition comprising a diene rubber such as butadiene rubber or the like, an organic peroxide, and an unsaturated carboxylic acid or a metal salt thereof and may be either a single-layered core or a multi-layered core having at least two layers. The wound core is a core where the rubber sphere is wound with a rubber thread.

The core has a diameter of 36.8 to 41.8 mm, preferably 37.8 to 41.4 mm.

The solid golf ball of the present invention is constructed by combining such a core with the aforementioned polyurethane cover. The cover may be single-layered or multi-layered. In the case of a multi-layered cover, it is required that at least one layer thereof consist of the polyurethane cover according to the present invention. Further, the golf ball of the present invention is usually provided with paint finish, a marking stamp and the like to enhance the appearance and commercial value thereof before it is put on the market.

[EXAMPLES]

[Measurement and Evaluation Methods]

1. Hardness

The hardness was measured by applying a spring hardness tester D-type prescribed by ASTM-D2240 to a non-dimpled portion of the surface of the golf ball.

2. Initial Repulsion Index

An aluminum cylindrical body having a weight of 198.4 g was allowed to impinge upon each golf ball at a velocity of 45 m/sec. The respective velocities of the cylindrical body and the golf ball before and after the impingement were measured, and the repulsion coefficient of each golf ball was calculated from the respective velocities thus measured and the respective weights. The measurement was performed five times for each golf ball and the average of the measured values was calculated.

The repulsion coefficient of each golf ball was reduced to an index number assuming that the repulsion coefficient of golf ball No. 1 shortly after manufactured was 100. A greater repulsion index is indicative of a higher repulsion property.

3. Heat Resistance

Each golf ball as manufactured was allowed to stand in an oven at 70°C for one week and then the repulsion coefficient was determined in accordance with the initial repulsion index measuring method. The repulsion coefficient thus measured was reduced to an index number assuming that the initial repulsion coefficient of golf ball No. 1 shortly after manufactured was 100.

4. Weather resistance

Each golf ball as manufactured was subjected to 120 hour-irradiation in a sunshine weatherometer and then the repulsion coefficient was determined in accordance with the initial repulsion index measuring method. The repulsion coefficient thus measured was reduced to an index number assuming that the initial repulsion coefficient of golf ball No. 1 shortly after manufactured was 100.

5. Water Resistance

Each golf ball as manufactured was allowed to stand in water at 60°C for one week and the repulsion coefficient was determined in accordance with the initial repulsion index measuring method. The repulsion coefficient thus measured was reduced to an index number assuming that the initial repulsion coefficient of golf ball No. 1 shortly after

manufactured was 100.

6. Shot feeling

The shot feeling of each golf ball shortly after manufactured was evaluated in the following manner. Ten top-level amateur golfers actually hit each golf ball with a metal head driver W#1. Each golfer judged each golf ball to be good or bad synthetically in view of the impact strength upon a shot and a sensation of repulsion imparted thereby. Each golf ball was rated in such a level that "○" is the case that less than two golfers judged the golf ball to be bad, "△" is the case that two to five golfers judged the golf ball to be bad, and "×" is the case that at least six golfers judged the golf ball to be bad.

[Influence of the polyol component constituting a urethane prepolymer]

(1) Manufacture of Solid Core

The rubber composition of the formulation shown in Table 1 was vulcanized and molded at 160°C for 30 minutes, to form a spherical solid core having a diameter of 40.0 mm.

In Table 1, butadiene rubber is "high-cis polybutadiene BR-01 (cis content: 96%)" produced by JSR Corp.; zinc acrylate is "ZNDA 90S" produced by

NIPPON JYORYU CO.; zinc oxide is "Toho Zinc oxide No.1"; and dicumyl peroxide is one produced by NOF Corp.

Table 1

(2) Synthesis of Prepolymer

4,4'-diphenylmethane diisocyanate (produced by Nippon Polyurethane Industry Co.) was mixed with a polycarbonate diol represented by the following formula (produced by UBE Industries), polytetramethylene ether glycol (produced by BASF JAPAN Co.) or poly(ethylene adipate) glycol (produced by Sanyo Chemical Ind.) having respective number-average molecular weight shown in Table 2 in a blending molar ratio between the NCO group and the OH group (NCO/OH) of 4/1. The resulting mixture was reacted at 70°C for 3 hours in a nitrogen atmosphere while being stirred. Thus, isocyanate-terminated urethane prepolymers having respective NCO contents (% by mass) and respective number-average molecular weights shown in Table 2 were each synthesized.

[Formula 2]

(3) Manufacture of Cover

The isocyanate-terminated urethane prepolymer thus synthesized was mixed with 1,4-butanediol (produced by BASF JAPAN Co.) in an amount such that

the molar ratio(OH/NCO) of the hydroxyl group of the curing agent to the isocyanate group of the urethane prepolymer is 1.05. Further, titanium oxide was added in an amount of 2 parts by mass to 100 parts by mass of the total of the urethane prepolymer and the curing agent, to prepare a viscous liquid of a cover composition.

The cover composition thus prepared was injected into a hemispherical mold formed with convex portions for forming dimples in which the previously manufactured core was held, and then this mold was inverted and mated with another hemispherical mold (also formed with convex portions for forming dimples) containing the cover composition injected thereinto, followed by press molding at 80°C for 15 minutes to cure.

After the curing, the resulting golf ball was removed from the molds, deburred, and then coated with a white paint and further with a clear paint on the surface thereof to obtain golf balls Nos. 1 to 7 each having a diameter of 24.8 mm and a mass of 45.2 to 45.7 g.

Golf ball No. 8 was manufactured in the same manner as with golf ball No. 2 except that Elasmer 250P was used as the curing agent. Elasmer 250P is

polytetramethyleneoxide aminobenzoate (amine value: 249.4 mgKOH/g) produced by Ihara Chemical Ind.

According to the evaluation methods described above, each golf ball shortly after manufactured was evaluated as to its hardness, repulsion property and shot feeling. Further, the heat resistance test, weather resistance test and water resistance test were conducted on each golf ball according to the evaluation methods described above. The results along with the composition of each urethane prepolymer are shown in Table 2.

Table 2

Golf ball No. 6 manufactured by using polytetramethylene ether glycol (PTMG) as the polyol component exhibited an initial repulsion index of 100, which was equal to the initial repulsion index of golf ball No. 1 as an working example of the present invention. However, the repulsion index of golf ball No. 6 after any one of the heat resistance test, weather resistance test and water resistance test was inferior to that of golf ball No. 1. Thus, golf ball No. 6 was inferior in repulsion durability. Golf ball No. 7 manufactured by using poly(ethylene adipate) as the

polyol component exhibited a particularly lowered repulsion index after the water resistance test.

From comparison among golf balls Nos. 1 to 5 each manufactured by using a polycarbonate diol as the polyol component, it was found that the initial repulsion property was lowered when the molecular weight was either too small (golf ball No. 4) or too large (golf ball No. 5). Golf ball No. 4, in particular, exhibited a lowered repulsion property in spite of its increased height. Since the polyol component forming a urethane prepolymer is considered to serve as a soft segment, it is conceived that the polyol component is required to have a large molecular weight to a certain extent so as to impart a golf ball with a satisfactory repulsion property.

[Influence of the free NCO content of a urethane prepolymer]

(1) Manufacture of Solid Core

The rubber composition of the formulation shown in Table 1 was vulcanized and molded at 160°C for 30 minutes, to form a spherical solid core having a diameter of 40.0 mm.

(2) Preparation of Urethane Prepolymer

4,4'-diphenylmethane diisocyanate (produced

by Nippon Polyurethane Industry Co.) was mixed with a polycarbonate diol (produced by UBE Industries) having a number-average molecular weight of 1987 at a mixing molar ratio (MDI:PCG) varied as shown in Table 3, to prepare isocyanate-terminated urethane prepolymers Nos. 11 to 15 having respective NCO contents (% by mass) and respective number-average molecular weights shown in Table 3.

(3) Manufacture of Cover

Each of the isocyanate-terminated urethane prepolymers thus synthesized was mixed with 1,4-butanediol (produced by BASF JAPAN Co.) in an amount such that the molar ratio of the hydroxyl group of the curing agent to the isocyanate group of the urethane prepolymer (OH/NCO) is 1.05. Further, titanium oxide was added in an amount of 2 parts by mass to 100 parts by mass of the total of the urethane prepolymer and the curing agent to prepare a viscous liquid of cover compositions.

In the same manner as golf ball No. 1, golf balls Nos. 11 to 15 were manufactured using each of the cover compositions thus prepared and the core manufactured as described above.

According to the evaluation methods described above, each golf ball shortly after manufactured was

evaluated as to its hardness, repulsion property and shot feeling. Further, the heat resistance test, weather resistance test and water resistance test were conducted on each golf ball according to the evaluation methods described above. The results along with the composition of each urethane prepolymer are shown in Table 3.

Table 3

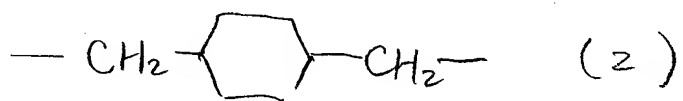
The urethane prepolymer having a low free isocyanate content gave an inferior initial repulsion property and a poor shot feeling to the golfers(No.12), because it is presumably considered that the obtained polyurethane cover has a lowered crosslinking density and becomes soft. On the other hand, the initial repulsion property became higher as the free isocyanate content of a urethane prepolymer increased. However, when the free isocyanate content was more than 15% by mass, the shot feeling was too bad for practical use(No.15).

[Effect of the invention]

The golf ball of the present invention uses a polycarbonate polyol that is excellent in heat resistance, weather resistance and water resistance as a constituent of the polyurethane cover, and hence exhibits superior durability and maintains a

high repulsion property.

[1K 1]



[1K 2]

